



# Technical Note: Quantification of interferences of wet chemical HONO measurements under simulated polar conditions

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# Technical Note: Quantification of interferences of wet chemical HONO measurements under simulated polar conditions

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## Interferences of wet chemical HONO measurements

J. Kleffmann and  
P. Wiesen

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

## Abstract

In the present pilot study, an optimized LOPAP instrument for the detection of nitrous acid (HONO) in the atmosphere (DL 0.2 pptV) was tested at the high alpine research station “Jungfrauoch” at 3580 m altitude in the Swiss Alps under conditions comparable to polar regions. HONO concentrations in the range <0.5–50 pptV with an average of 7.5 pptV were observed at the “Jungfrauoch”. The diurnal profiles obtained exhibited clear maxima at noon and minima with very low concentration during the night supporting the proposed photochemical production of HONO. In good agreement with recent measurements at the South Pole, it was demonstrated, that interferences of chemical HONO instruments can significantly influence the measurements and lead to considerable overestimations, especially for low pollution level. Accordingly, the correction of interferences is of paramount importance for those instruments, which sample HONO on aqueous or humid surfaces.

## 1 Introduction

Nitrous acid (HONO) is an important source of the OH radical, the primary oxidant in the atmosphere:



While historically, HONO was considered to be of high importance only in the early morning (Harris et al., 1982; Calvert et al., 1994; Harrison et al., 1996; Volkamer et al., 2007), most recent measurements indicate a significant contribution to the OH production also later during the day (Li, 1994; Neftel et al., 1996; Staffelbach et al., 1997; Zhou et al., 2001; Yang et al., 2002; Vogel et al., 2003; Kleffmann et al., 2005; Acker et al., 2006a, b), which is explained by photochemical sources (Kleffmann, 2007). Especially in polar regions, unexpected high HONO levels have been observed during sunlight over snow surfaces (Li, 1994; Zhou et al., 2001; Beine et al., 2001, 2002;

ACPD

8, 3497–3523, 2008

## Interferences of wet chemical HONO measurements

J. Kleffmann and  
P. Wiesen

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Dibb et al., 2002, 2004; Honrath et al., 2002; Jacobi et al., 2004; Amoroso et al., 2006). It was estimated that the photolysis of HONO can be the dominant source of OH radicals for these regions and possibly controls the oxidation capacity of the lower polar atmosphere (Li, 1994; Zhou et al., 2001; Yang et al., 2002). Accordingly, the mechanistic understanding and quantification of HONO sources over irradiated snow surfaces is of paramount importance.

However, the mechanisms of HONO formation in polar regions are not well understood at present. It was proposed (Zhou et al., 2001; Beine et al., 2001, 2002; Dibb et al., 2002; Honrath et al., 2002) that HONO formation is caused directly by the photolysis of nitrate on snow surfaces (Dubowski et al., 2002), which can also explain observed NO<sub>x</sub> emissions (for example: Honrath et al., 1999; Cotter et al., 2003; Jacobi et al., 2007). The photolysis of nitrate was proposed, since for example, the photolytic formation of HONO correlates with the calculated photolysis frequency of nitrate (Honrath et al., 2002) and with the concentration of nitrate in snow (Dibb et al., 2002). However, recent laboratory studies and accompanying modelling imply very low direct HONO yields and formation by secondary heterogeneous chemistry, for example via the primary formed NO<sub>2</sub> (Jacobi et al., 2007). Such secondary chemistry was also proposed to explain the absence of significant HONO formation from nitrate containing snow in Antarctic coastal regions, for which HONO formation should have been observed based on the proposed nitrate mechanism (Beine et al., 2006). One of the proposed secondary reactions on snow surfaces is the recently observed reduction of NO<sub>2</sub> with photo-sensitized organic compounds, for example fulvic and humic acids (George et al., 2005; Stemmler et al., 2006, 2007). The reaction is orders of magnitude faster than the heterogeneous disproportionation of NO<sub>2</sub> with water on humid surfaces (Finlayson-Pitts et al., 2003), which was proposed earlier to explain high HONO yields over snow surfaces (Zhou et al., 2001). Caused by the much faster kinetics and the ubiquitous presence of organic compounds in polar regions (Grannas et al., 2004, 2007), this mechanism may help to explain strong HONO formation and the high observed HONO/NO<sub>x</sub> ratios, which is in contrast to laboratory studies about the

## Interferences of wet chemical HONO measurements

J. Kleffmann and  
P. Wiesen

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

nitrate photolysis (Zhou et al., 2001; Jacobi et al., 2007). However, verification of this mechanism for polar regions is still an important open issue.

Measurements of gaseous HONO have been made since many years in the atmosphere with various techniques (for example: Platt et al., 1980; Ferm and Sjödin, 1985; Kanda and Taira, 1990; Večeřa and Dasgupta, 1991; Zhou et al., 1999; Heland et al., 2001; Liao et al., 2006). In addition to the only very recently applied optical LIF technique (Liao et al., 2006), only carbonate denuders (Li, 1994; Beine et al., 2001), mist chambers (Dibb et al., 2002; Honrath et al., 2002) and the HPLC technique (Zhou et al., 2001; Beine et al., 2002, 2006) have been used for polar HONO measurements up to now. The common principle of these her called “chemical instruments” is the sampling of HONO on humid or aqueous surfaces in the form of nitrite. However, it is well known that many heterogeneous reactions lead to the formation of nitrite on similar surfaces. One of these reactions, which is typically not considered, is the recently observed fast reduction of NO<sub>2</sub> with adsorbed hydrocarbons (Gutzwiller et al., 2002; Kleffmann et al., 2002) during sampling of HONO. In addition, for polar measurements interference by HO<sub>2</sub>NO<sub>2</sub> was proposed (Liao et al., 2006; Clemitshaw, 2006). Chemical interferences were recently observed and quantified for atmospheric HONO measurements by a LOPAP instrument and were demonstrated to correlate inversely with the pollution level (Kleffmann et al., 2006). Accordingly, these interferences may be of particular importance for polar measurements, however, are typically not corrected for by the used chemical instruments. Besides interferences, artificial heterogeneous HONO formation (for example: Kleffmann et al., 1998; Zhou et al., 2002) in sampling lines of up to 30 m length, used for polar measurements (see for example: Zhou et al., 2001), may affect the accuracy of the data.

Caused by these potential problems and by results from modelling of experimental HONO, NO<sub>x</sub> and HO<sub>x</sub> data, polar HONO measurements were considered to be too high (Chen et al., 2004; Sjøstedt et al., 2005; Bloss et al., 2006; Grannas et al., 2007; Sjøstedt et al., 2007). This was recently confirmed by the first polar HONO intercomparison study, in which a mist chamber instrument measured on average 7 times higher HONO

## Interferences of wet chemical HONO measurements

J. Kleffmann and  
P. Wiesen

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

values than a LIF instrument (Liao et al., 2006). It is worth mentioning that higher HONO values were typically also measured by chemical instruments in other intercomparison studies against the optical DOAS technique under rural and urban conditions, especially during daytime for low HONO concentrations (Appel et al., 1990; Coe et al., 1997; Müller et al., 1999; Wiesen, 2002; Spindler et al., 2003). Although it is evident that chemical instruments most probably overestimate HONO concentrations in polar regions, still data from these type of instruments are published and used for the interpretation of polar atmospheric processes (Jones et al., 2007).

In conclusion, there is an urgent need for the exact quantification of HONO concentrations in polar regions by instruments free of interferences and sampling artefacts leading to a better understanding of the impact of HONO on the oxidation capacity of the polar atmosphere. Thus, the pilot study presented here was aimed to demonstrate that the recently developed LOPAP instrument for the detection of HONO in the atmosphere is capable to work also under polar atmospheric conditions. In addition, quantification of interferences, which are measured and corrected for by this instrument, should demonstrate the potential problems of chemical HONO measurements, especially for low pollution levels. To simulate polar atmospheric conditions, HONO measurements were performed on the easy accessible high alpine research station “Jungfrauoch” during the period 2–7 November 2005.

## 2 Experimental

### 2.1 LOPAP instrument

Nitrous acid (HONO) was measured with a very sensitive instrument (LOPAP), which is described in detail elsewhere (Heland et al., 2001; Kleffmann et al., 2002). In addition, most recent modifications are specified in a recent intercomparison paper (Kleffmann et al., 2006). Briefly, HONO is first sampled in a temperature controlled (20°C) double-wall stripping coil by a fast chemical reaction in the stripping reagent, which is a mixture

## Interferences of wet chemical HONO measurements

J. Kleffmann and  
P. Wiesen

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

of sulphanilamide in hydrochloric acid (10 g/L, 1N). Caused by a very fast chemical reaction, a very short stripping coil (17 cm length, 2 mm i.d.) is used to obtain a 99.4% uptake for 1.5 L/min gas flow used in the present study, resulting in a very short contact time of interfering substances with the liquid surface. The sampling conditions used for the LOPAP instrument have the advantage that HONO is completely sampled at low pH, for which several known chemical interferences caused by e.g. NO<sub>2</sub> and SO<sub>2</sub> (Littlejohn et al., 1993; Spindler et al., 2003), NO<sub>2</sub> and phenols (e.g. Alfassi et al., 1986; Coombes et al., 1994; Ammann et al., 2005), NO<sub>2</sub>+aromatic amines (Saltzman, 1954) or PAN hydrolysis (Frenzel et al., 2000) are minimised (Heland et al., 2001; Kleffmann et al., 2002, 2006).

The stripping coil is mounted in an external temperature controlled sampling unit, which is placed directly in the atmosphere of interest, excluding the use of any sampling lines. Thus, sampling artefacts in sampling lines, i.e. heterogeneous formation on surfaces by e.g. different NO<sub>2</sub> reactions (e.g. Gutzwiller et al., 2002; Finlayson-Pitts et al., 2003; Ammann et al., 2005), photolytic formation on surfaces (Zhou et al., 2002), or condensation of analytes on inlet surfaces (Keene et al., 2006) are minimised. After the separation from the gas phase, the stripping reagent is pumped through an isolated temperature controlled reagent line to the instrument, where it is converted into an intensively coloured azo dye by the reaction with N-naphtylethyldiamine-dihydrochloride (Grasshoff et al., 1983). The absorption of the light from a white light-emitting diode (LUXEON) by the dye is measured in long path absorption tubes made of Teflon<sup>®</sup> AF 2400 using a minispectrometer (Ocean Optics, SD 2000). The light from and to the absorption tubes is transferred by glass fibre optics (200 µm). All continuous liquid flows are adjusted by a peristaltic pump (Ismatec). The light spectra are stored and processed by a mini computer and the absorbance can be continuously followed on the computer.

In the external sampling unit two similar stripping coils are connected in series to correct for interferences, which are expected for chemical HONO instruments (Appel et al., 1990; Spindler et al., 2003; Liao et al., 2006). In the first stripping coil HONO

## Interferences of wet chemical HONO measurements

J. Kleffmann and  
P. Wiesen

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

is almost quantitatively sampled (see above). Thus, the signal in the second channel results only from interfering substances, like e.g.  $\text{NO}_2$ . Under the assumption, that the interfering substances are taken up only by a small amount in each coil, the difference between the signals in channel 1 and 2 gives the interference free HONO signal. Caused by this two channel approach, all tested interferences against  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{NO}+\text{NO}_2$ ,  $\text{N}_2\text{O}_5$ ,  $\text{HNO}_3$ ,  $\text{HNO}_3+\text{HCHO}$ ,  $\text{O}_3$ ,  $\text{O}_3+\text{HONO}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{O}_2+\text{HONO}$ ,  $\text{SO}_2$ ,  $\text{SO}_2+\text{NO}_2$ , PAN, alkyl nitrates, phenols+ $\text{NO}_2$ ,  $\text{NO}_2$ +diesel exhaust, interferences from complex photo smog mixtures and from sub-micron particles are either not measurable or can be corrected for (Heland et al., 2001; Kleffmann et al., 2002, 2006; Bröske et al., 2003). This is also confirmed by recent intercomparison campaigns of this instrument against the DOAS technique in the field and in a large outdoor simulation chamber, for which excellent agreement was obtained for the same air masses also for daytime conditions, although interferences were often significant but could be corrected by the measurement principle (Kleffmann et al., 2006).

To correct for small zero drifts, regular automatic zero measurements of 20 min each 4 h were performed during the campaign. To avoid significant “extra” surfaces in the inlet, the zero air was injected directly into the inlet of the stripping coil by a 16” PFA line with a slightly higher flow rate than that of the instrument. The instrument was calibrated two times, at the beginning and at the end of the campaign to ensure constant sensitivity ( $\pm 5\%$ ). Using an optical path length of 6 m in this study, the instrument has a detection limit of 0.2 pptV for a response time of 7 min (10–90% of final signal), see Fig. 1. Since HONO concentrations near the detection limit cannot be easily generated by a HONO source, the signal of channel 2 of the instrument is also shown in Fig. 1 during the addition of  $\sim 20$  pptV of HONO. The data in channel 2 reflect chemical interferences and HONO, which is not sampled in channel 1. Since in the atmosphere HONO is determined from the difference of two channels, a detection limit of 0.2 pptV can be derived from the data shown for channel 2, which is in excellent agreement with the  $2\sigma$  noise of zero measurements during the field campaign at the Jungfraujoch. The accuracy and precision of the instrument are 7% (+DL) and 1% (+DL), respectively.

## Interferences of wet chemical HONO measurements

J. Kleffmann and  
P. Wiesen

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)



## 2.2 Location and weather conditions

The high altitude research station “Jungfrauoch” (7°59′2″ E, 46°32′53″ N, 3580 m altitude), which is a Global Atmosphere Watch (GAW) station, is located between the mountains “Jungfrau” and “Mönch” in Switzerland. Measurements were performed at the “Sphinx” building, which is surrounded by large snow and ice fields. Although the station is located in middle Europe, recent NO<sub>y</sub> measurements showed that the air reaching the station could be often compared with measurements at remote stations (Zellweger et al., 2003). Caused by the large snow and ice fields, the temperature range during the campaign and the low pollution level, the “Jungfrauoch” is considered as an ideal test site for polar measurements, but is much better accessible. Especially, when south-easterly winds were prevailing during three days of the campaign, the air flow was coming from the large glacier “Aletschglletscher” directly to the sampling port of the LOPAP instrument and thus, was in contact with large ice surfaces and not influenced by possible local emissions from the station.

The LOPAP instrument was installed in the GAW laboratory room below the roof of the “Sphinx” building. The external sampling unit was fixed on a plate ca. 1 m in front of a window on the east-north-east side of the building, ca. 8 m above the visitor’s platform. For three days the sampling unit was upwind and for two days it was downwind of the building. Since no significant difference in the HONO/NO<sub>y</sub> ratio could be observed between these two periods, artificial heterogeneous formation on surfaces of the building was considered to be of minor importance.

During the campaign the weather conditions varied significantly including clear sky, snowfall and presence of super-saturated cloud droplets leading to strong frost needle formation on all surfaces. The temperature varied between −9.2 and +0.9°C, the wind speed between 0–15 m/s and the pressure between 657–664 mbar.

### Interferences of wet chemical HONO measurements

J. Kleffmann and  
P. Wiesen

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

### 3 Results and discussion

#### 3.1 Experimental field data

The HONO concentration varied between  $<0.5$ – $50$  pptV (see Fig. 2) with a mean value of  $7.5$  pptV, which is in the same range compared to polar measurements (Li, 1994; Zhou et al., 2001; Beine et al., 2001, 2002; Dibb et al., 2002; Honrath et al., 2002) but also to measurements on other high altitude mountain sites (Kleffmann et al., 2002; Huang et al., 2002; Beine et al., 2005). The measured  $\text{NO}$ ,  $\text{NO}_2$  and  $\text{NO}_y$  concentrations were in the range  $0$ – $0.22$  ppbV,  $0$ – $0.75$  ppbV and  $0.3$ – $1.6$  ppbV, respectively (see Fig. 2).

The HONO concentration showed a strong diurnal variation with highest concentrations during daytime, strongly correlating with the irradiance (see Fig. 3). This observation is in good agreement with other measurements on mountain sites (Kleffmann et al., 2002; Huang et al., 2002; Acker et al., 2006a; Zhou et al., 2007), but also in polar regions and is explained by photochemical sources. For all data an average diurnal HONO profile was calculated from the 10 min mean values of the instrument (see Fig. 3). Average night-time (06:00–18:00) and noon time (12:00–13:00) HONO concentration of  $\sim 3.5$  pptV and  $\sim 17$  pptV were observed. The variability of the data is lower during the night compared to the day. This might be explained by a decreasing boundary layer height during the night and a much lower influence of the variable pollution from the valleys around the measurement site during the night, in addition to the absence of local photochemical sources. Accordingly, the mean night-time concentration of  $3.5$  pptV is considered as the upper limit HONO concentration in the free troposphere during night in mid Europe. The high daytime concentrations are most probably caused by fast photolytic formation of HONO, since the diurnal HONO profile nicely matches with the variation of the irradiation (Fig. 3). However, since photolytic HONO formation is proposed by heterogeneous processes on ground surfaces and since the lifetime of HONO during the day is only  $\sim 10$  min, it should be pointed out that these high values are not representative for the free troposphere during the day.

### Interferences of wet chemical HONO measurements

J. Kleffmann and  
P. Wiesen

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The mean diurnal HONO/NO<sub>x</sub> and HONO/NO<sub>y</sub> ratios varied between 0.5–26% (mean: 4.6%) and 0.2–4% (mean: 1.1%), respectively, with the low values during night-time and the high values around noon (see Fig. 3). These values are in good agreement with mean values of HONO/NO<sub>x</sub>=2.5% and HONO/NO<sub>y</sub>=1.0%, respectively, measured by a LOPAP instrument at the high altitude mountain site Zugspitze (2650 m altitude, unpublished data from Kleffmann et al., 2002). However, the mean HONO/NO<sub>x</sub> ratio determined by the LOPAP instrument is much lower than for other field campaigns on high mountain sites, for which mean values of ~30% (Huang et al., 2002) and 23% (Zhou et al., 2007) were reported by other chemical instruments. In addition, also during polar field campaigns very high ambient HONO/NO<sub>x</sub> ratios of ~25% (Beine et al., 2001; Jacobi et al., 2004) up to ~100% (Jones et al., 2007) were determined. These high values may be explained by significant chemical interferences, which are normally not corrected for by chemical instruments in contrast to the LOPAP instrument (see below).

The average diurnal HONO concentration was highly correlated with the irradiance ( $R^2=0.83$ ) and the product (irradiance $\times$ 1/wind speed) ( $R^2=0.88$ ), confirming the proposed photochemical formation on ground surfaces. In addition, HONO was moderately correlated with NO ( $R^2=0.58$ ). However, there was not any positive correlation of HONO with NO<sub>2</sub>, NO<sub>y</sub> or NO<sub>z</sub>. Accordingly, based on the experimental observations, the mechanism of the photolytic daytime HONO formation, i.e. nitrate photolysis (Zhou et al., 2001; Beine et al., 2001, 2002; Dibb et al., 2002; Honrath et al., 2002) versus photo-sensitized NO<sub>2</sub> reduction on organic surfaces (George et al., 2005; Stemmler et al., 2006, 2007), remains still an important open question, however, its clarification was not the objective of this pilot study.

### 3.2 Interferences

In the LOPAP instrument two channels are used to correct for interferences. While HONO is almost completely taken up by a very fast selective chemical reaction in the first channel, other tested interfering gases pass the first coil nearly unaffected (see

## Interferences of wet chemical HONO measurements

J. Kleffmann and  
P. Wiesen

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



above). This can be explained by a saturation of a thin surface layer of the sampling reagent and a liquid phase diffusion limited uptake of interfering gases, which are taken up only driven by their solubility. In contrast, caused by the extremely high excess of the reactant sulfanilamide, each colliding HONO is taken up by a chemical reaction in the sampling solution of the LOPAP instrument. Thus, it is proposed, and confirmed for all tested interferences in the laboratory (see above), that the interference signal is similar in both channels. Accordingly, the difference channel 1 – channel 2, corrected for the small HONO losses in the first channel, gives the interference free HONO concentration. This is confirmed by the excellent agreement with DOAS measurements under very complex conditions in the atmosphere and in a smog chamber (Kleffmann et al., 2006). It should be pointed out that interferences are expected to be of even higher importance for other chemical instruments, caused by the longer contact time of the gas phase in their sampling devices compared to the LOPAP instrument (~30 ms). For example, the recently observed interfering compounds from diesel exhaust were found to be completely removed by a wetted effluent diffusion denuder (Gutzwiller et al., 2002), while only small, correctable uptake was observed for the LOPAP instrument (Kleffmann et al., 2002). In addition, since the kinetics of known interfering liquid phase reactions, i.e. PAN hydrolysis (Frenzel et al., 2000), NO<sub>2</sub>+SO<sub>2</sub> (Littlejohn et al., 1993; Spindler et al., 2003), NO<sub>2</sub>+phenols (Alfassi et al., 1986; Coombes et al., 1994; Ammann et al., 2005) or NO<sub>2</sub>+aromatic amines (Saltzman, 1954), increase with increasing pH, chemical interferences are expected to be even more severe for instruments, which collect air samples under neutral or even basic conditions (see for example, Spindler et al., 2003; Genfa et al., 2003). In contrast, in the LOPAP instrument very acidic sampling conditions are applied (pH=0).

Also from most known intercomparison studies, it can be inferred that interferences are a general problem of chemical instruments (Appel et al., 1990; Coe et al., 1997; Müller et al., 1999; Spindler et al., 2003; Wiesen, 2002; Liao et al., 2006), for which the chemical instruments typically measured significantly higher concentrations than the optical instruments, especially during daytime. The difference was explained by

## Interferences of wet chemical HONO measurements

J. Kleffmann and  
P. Wiesen

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

interferences of the chemical instruments (e.g. Appel et al., 1990; Spindler et al., 2003; Liao et al., 2006). However, there are two other intercomparison studies, for which good agreement was reported between the DOAS technique and chemical instruments, which do not correct for interferences (Acker et al., 2006b; Keene et al., 2006). In the study of Keene et al. (2006) the sum of the ion chromatography signal from nitrite and nitrate were inferred as HONO for the used mist chamber instrument, since the samples were analysed several hours after sampling, for which nitrite to nitrate conversion was observed. Thus, any atmospheric  $\text{HNO}_3$  or  $\text{N}_2\text{O}_5$  is inferred as HONO in this study. In addition, the authors reported problems with condensation of analytes on inlet surfaces, which they tried to correct for by rinsing these surfaces with water and correcting in their calculations, leading to additional uncertainties by inlet artefacts. And finally, half of the data points were below the detection limit of the DOAS. Caused by these uncertainties the HONO data were considered being semi-quantitative by the authors (Keene et al., 2006). Thus, the reported data should not be used to disprove the existence of interferences of chemical instruments.

In another recent study of Acker et al. (2006b) good agreement was reported between an HPLC, a WEDD and a DOAS system for field measurements in Rome as part of the European NITROCAT project. However, when looking in detail to the data presented in the corresponding final project report (Wiesen et al., 2002) for 11 of 17 simultaneous days the HPLC system measured significantly higher values (up to a factor of 4) than the DOAS instrument during daytime, while the night-time values were on average in good agreement. Similar observations with consistent night-time but higher daytime values of chemical instruments compared to the DOAS technique were already reported in other intercomparison studies (Appel et al., 1990; Müller et al., 1999; Spindler et al., 2003). These results are also in agreement with relative interference measurements of the LOPAP instrument in many field campaigns, for which typically low relative interferences are measured during night-time but significant correction has to be applied for low HONO concentrations during daytime (Kleffmann et al., 2006). In conclusion, the significantly higher daytime values of the HPLC instrument compared

## Interferences of wet chemical HONO measurements

J. Kleffmann and  
P. Wiesen

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

to the DOAS technique for the NITROCAT campaign and similar observations from other intercomparison studies (see above) confirm the general importance of chemical interferences.

Caused by the fact that chemical interferences are expected to be of even higher importance for other instruments (see above), the data from the interference channel 2 of the LOPAP instrument from the present study was used to estimate the general importance of chemical interferences for remote measurements. Only, if the data from the LOPAP instrument is affected by yet unknown acid catalysed interferences, the results from the present study would be not representative for other chemical instruments. However, the excellent agreement of the interference corrected LOPAP data with the DOAS technique in the field and in a smog chamber (Kleffmann et al., 2006), the much lower HONO/NO<sub>x</sub> ratio of the LOPAP data compared to other high mountain site and polar measurements (see above) and the strong overestimation of other chemical instruments observed in most known intercomparison studies (see above) disprove this hypothesis.

While typically the correction of interferences was in the range 10–50% for the campaign at the “Jungfrauoch”, very high interferences of >100% were observed several times during the campaign (see Figs. 4 and 5). For the data shown in Fig. 4 the signal of the interference channel 2 was nearly as high as that of channel 1. The reason for these surprisingly high interferences is still unclear. The small and well-known interferences of the LOPAP instrument, for example against ozone and NO<sub>2</sub> (Kleffmann et al., 2002), can only explain a signal of ~1 pptV in channel 2 under the conditions shown in Fig. 4. In addition, there was not any correlation of the interference signal with the concentration of O<sub>3</sub> ( $R^2=0.009$ ), NO<sub>2</sub> ( $R^2=0.15$ , slope negative), NO<sub>y</sub> ( $R^2=0.27$ , slope negative). Thus, other unknown interferences, for example including oxidizable hydrocarbons (Alfassi et al., 1986; Coombes et al., 1994; Gutzwiller et al., 2002; Ammann et al., 2005), might explain the observed high signal in channel 2. The relative interference was found to increase with decreasing HONO-concentration (see Fig. 5), which is in excellent agreement with other field campaigns of the LOPAP instrument (Kleff-

## Interferences of wet chemical HONO measurements

J. Kleffmann and  
P. Wiesen

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

mann et al., 2006). This indicates that especially for remote conditions the correction of interferences is of paramount importance for the correct determination of HONO concentrations.

A strong correlation of the measured interference signal of channel 2 with the irradiance was also observed (see Fig. 6). This might be explained by the photochemical formation of interfering compounds, such as phenols, during daytime. In addition, it might also reflect the micrometeorological variations associated with surface heating by solar radiation, which could cause stronger upward transport of air masses containing higher concentrations of interfering compounds.

The results from the present study demonstrate the importance of using a two channel chemical instrument for the detection of nitrous acid in the atmosphere. Since it can be expected that also other chemical instruments will suffer from these interferences, it might be possible that several HONO measurements reported to date are afflicted with large errors, especially at low HONO concentrations. For example, during the night shown in Fig. 4, the HONO concentration would have been overestimated by a factor of up to 4, if only a one-channel LOPAP instrument had been used. This factor can be compared with the observed mean discrepancy of a factor of 7 between data from a one channel mist chamber instrument and an LIF instrument, which were recently reported from a campaign at the South Pole (Liao et al., 2006). Caused by the observed inverse dependency of interferences on the pollution level (see Fig. 5), both observations are in excellent agreement and demonstrate the necessity to verify recently published HONO data from polar regions by instruments free of artefacts.

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## Interferences of wet chemical HONO measurements

J. Kleffmann and  
P. Wiesen

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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## Interferences of wet chemical HONO measurements

J. Kleffmann and  
P. Wiesen

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





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## Interferences of wet chemical HONO measurements

J. Kleffmann and  
P. Wiesen

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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## Interferences of wet chemical HONO measurements

J. Kleffmann and  
P. Wiesen

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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## Interferences of wet chemical HONO measurements

J. Kleffmann and  
P. Wiesen

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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ACPD

8, 3497–3523, 2008

## Interferences of wet chemical HONO measurements

J. Kleffmann and  
P. Wiesen

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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ACPD

8, 3497–3523, 2008

## Interferences of wet chemical HONO measurements

J. Kleffmann and  
P. Wiesen

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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ACPD

8, 3497–3523, 2008

## Interferences of wet chemical HONO measurements

J. Kleffmann and  
P. Wiesen

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

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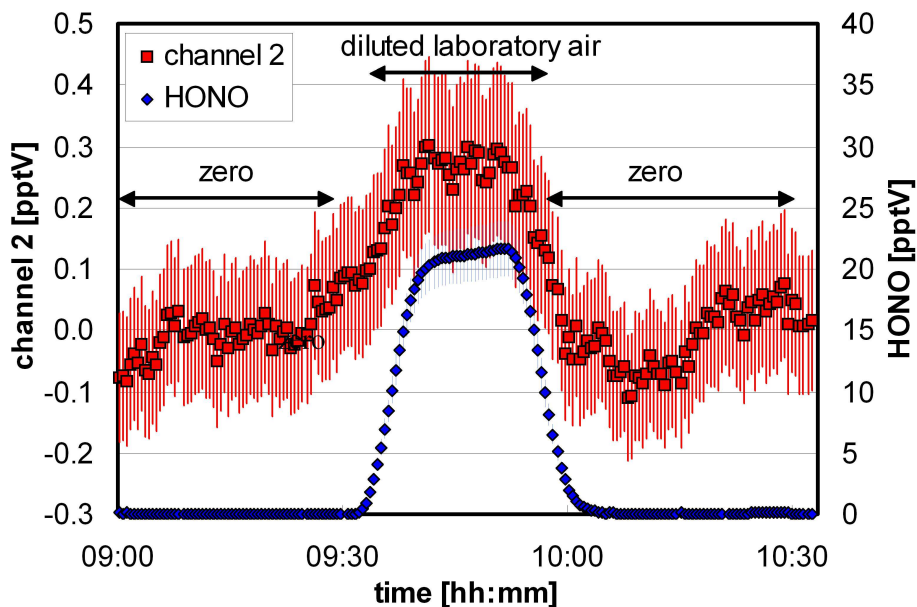
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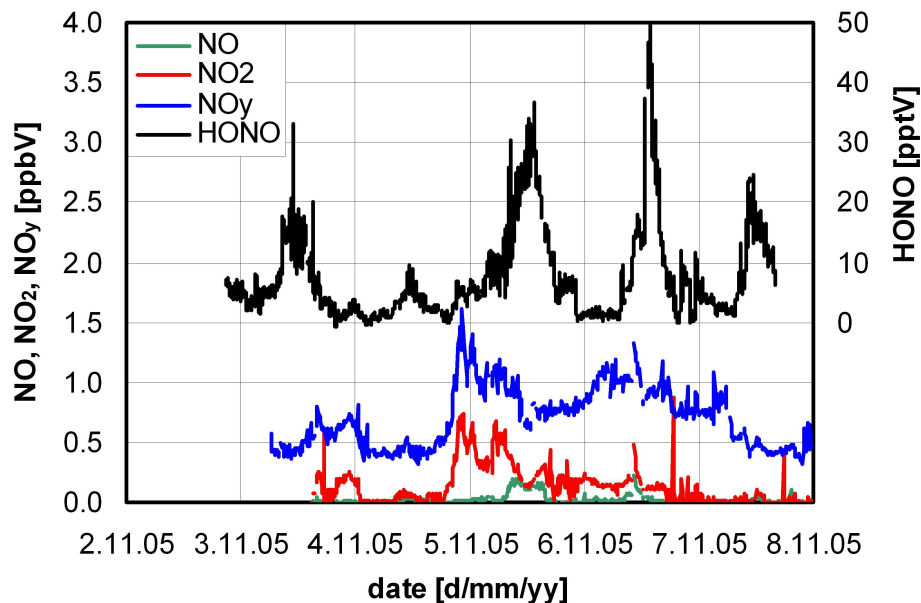


**Fig. 1.** Sensitivity tests of the optimized LOPAP instrument in the laboratory. For details see text.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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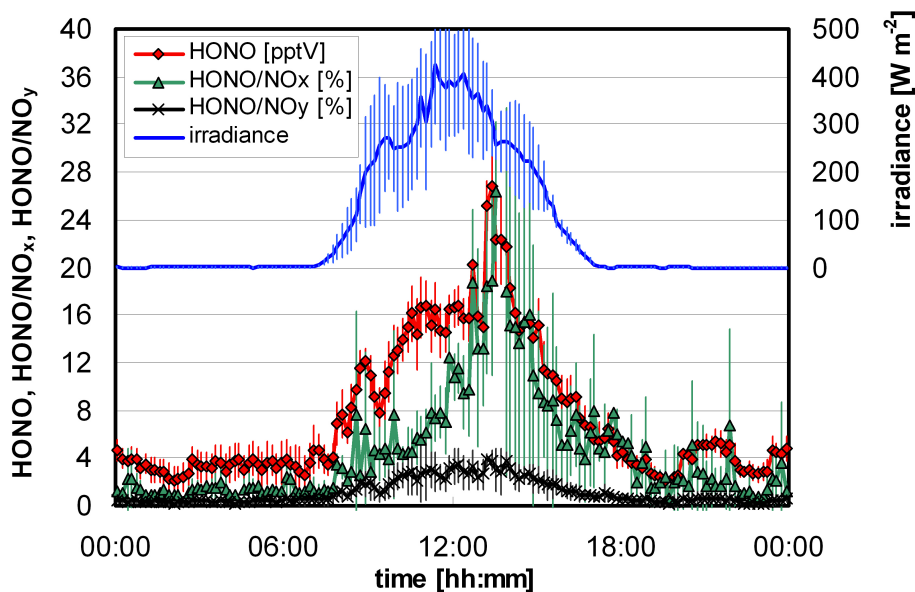
**Fig. 2.** HONO, NO, NO<sub>2</sub> and NO<sub>y</sub> concentrations during the field campaign at the “Jungfraujoch” (2–7 November 2005).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)



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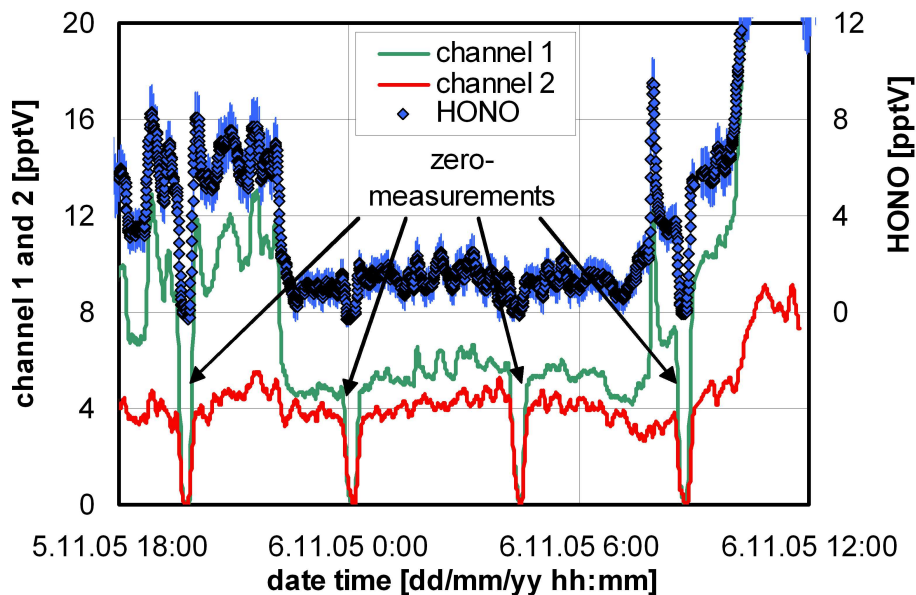


**Fig. 3.** Mean diurnal HONO concentration, HONO/NO<sub>x</sub>, HONO/NO<sub>y</sub> and irradiance (10 min averages) during the field campaign at the “Jungfrauoch”.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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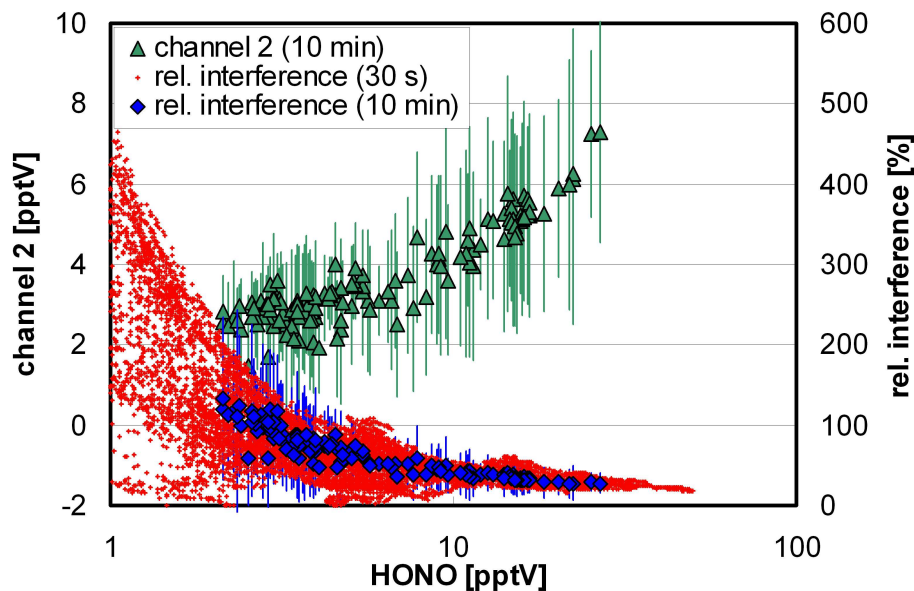


**Fig. 4.** Example of high interferences observed in the night 5–6 November 2005, leading to an overestimation of the HONO concentration of up to a factor of 4, if only a one channel instrument would be used.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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P. Wiesen

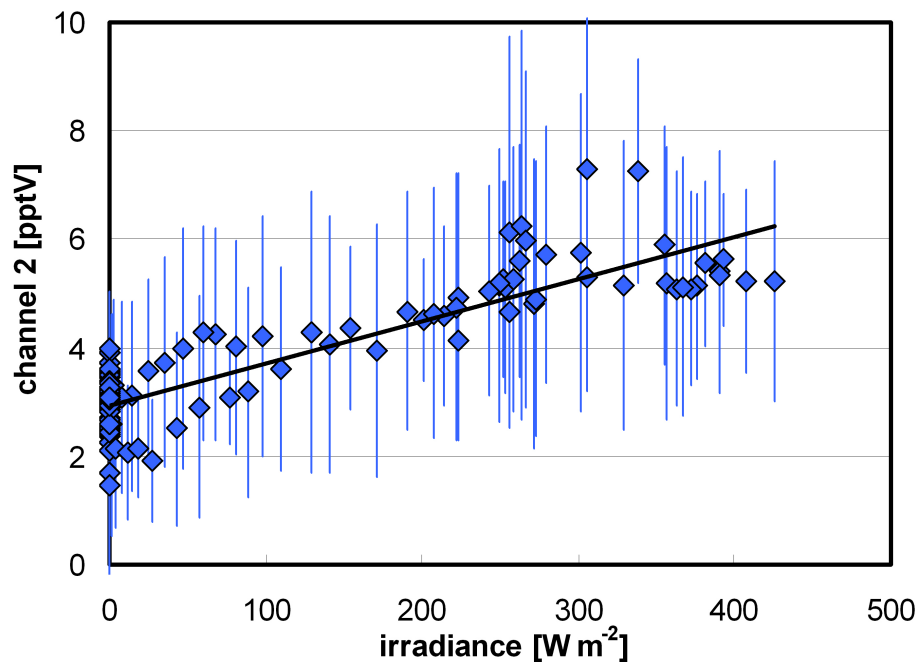


**Fig. 5.** Absolute interferences (channel 2) and relative interferences as a function of the HONO concentration for all data and for the average diurnal 10 min data during the campaign at the Jungfraujoch.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

**Interferences of wet  
chemical HONO  
measurements**

J. Kleffmann and  
P. Wiesen



**Fig. 6.** Plot of the average diurnal 10 min interference data from channel 2 against the irradiance during the campaign at the Jungfraujoch.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)